DEPARTMENT OF PHYSICS
SCHOOL OF SCIENCES AND HEALTH PROFESSIONS
OLD DOMINION UNIVERSITY
NORFOLK, VIRGINIA

Technical Report PTR-81-10

N_2 PRESSURE-BROADENED O_3 LINE WIDTHS AND STRENGTHS NEAR 1129.4 CM^{-1}

By

G. E. Copeland, Principal Investigator
L. N. Majorana
C. N. Harward
and
R. J. Steinkamp

Progress Report
For the period October 25, 1980 - October 24, 1981

Prepared for the
National Aeronautics and Space Administration
Langley Research Center
Hampton, Virginia 23665

Under
Research Grant NAG1-1
James M. Hoell, Technical Monitor
Instrument Research Division

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N_2 PRESSURE-BROADENED O_3 LINE WIDTHS AND STRENGTHS NEAR 1129.4 CM^{-1}

By

G.E. Copeland[1], L.N. Majorana[2], C.N. Harward[3], and R.J. Steinkamp[4]

ABSTRACT

A Beer's Law experiment was performed with a tunable diode laser to find the N_2 pressure-broadening characteristics of a single O_3 absorption line at 1129.426 cm^{-1} ($\nu 1$ Band, J, Ka, Kc = 31, 1, 31 ← 32, 0, 32) for N_2 pressures from 10 to 100 torr (O_3 pressure = 3.16 torr). SO_2 line positions were used for wavelength calibration. Line shapes were iteratively fitted to a Lorentz function. Results were δ(HWHM in MHz) = 47.44(±5.34) MHz + 1.730 (±0.088) MHz/torr *p(torr) with ρ = 0.9897. This intercept compares well with the Doppler O_3 - O_3 broadened (at 3.16 torr) width of 44.52 Hz (ref. 1). Any difference is most likely in laser frequency uncertainty. This results in a HWHM line width of 0.044 $cm^{-1} atm^{-1}$ at 760 torr and 285 K. The line strengths integrated over $\Delta\nu$=0.055 cm^{-1} were found to be N2 pressure dependent: $S(cm^{-2} torr^{-1}) = 1.334 \times 10^{-4} p(torr)^{-1.314}$ with ρ = -0.9957.

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INTRODUCTION

With the advent of semiconductor lasers and their recent application to spectroscopy (refs. 2-4), there has been a revolution in the study of infrared spectra. Use of the tunable diode laser (TDL) has permitted high-resolution (<0.0001 cm^{-1}) studies of several molecules of high current interest (ClO, HNO_3, SO_2, CF_2Cl_2, etc.). This study is concerned with the experimental determination of the pressure-broadened characteristics of a single O_3 line near 1129.4 cm^{-1}. This line has been suggested as a possible candidate for remote sensing experiments using either infrared heterodyne spectroscopy or differential lidar, since it is relatively well isolated from other atmospheric lines, has significant strength, and is relatively insensitive to temperature changes. A Beer's Law experiment is performed to determine the absorption coefficients and nitrogen (N_2) broadening parameters.

APPARATUS AND PROCEDURE

A simplified schematic of the apparatus is shown in figure 1. The radiation source is a PbSnTe TDL whose output is passed through collimating optics and a monochromator for mode selection. The output from the monochromator is divided by a beam splitter which directs 40 percent through a solid germanium etalon onto an LN_2-cooled HgCdTe detector. The remaining 60 percent is split into 2 beams. One beam is directed through a reference gas cell to a second detector and the other through the 50-cm O_3 absorption cell to a third detector. A more detailed description of the apparatus is to be found in the report by Majorana (ref. 5).

This arrrangement permits simultaneous recording of the O_3 absorption spectra, the etalon fringes for relative frequency calibration, and the SO_2 reference gas spectrum for conversion to absolute frequency (ref. 4). The detector output, the TDL current, and SO_2 and O_3 pressures were read by a 12-bit A/D and transferred to a 7-track tape by a PDP8/e minicomputer for later analysis. O_3 spectra were taken at 8 N_2 pressures (10-100 torr) at 285 K. SO_2 at 1 torr was used as the reference spectrum since a detailed atlas exists (ref. 6) The 1129.418 cm^{-1} line of SO_2 (ν_1, ν_2, ν_3, j,Ka,Kc)

[1,0,0,33,3,31 ← 0,0,0,34,2,32] was selected as the standard reference line because of its proximity to the O_3 line under study and the recent heterodyne confirmation of its position at 1129.41835 cm^{-1}.

THE DATA AND ITS ANALYSIS

The data were collected and processed in the same manner as described Majorana (ref. 5). Strip chart records were digitized and recorded on tape for later transfer to the ODU DEC System 10 computer. After input of data into the proper data format, each of the N_2-broadened O_3 profiles was processed using the program QUICK. One of the output products from program QUICK is a plot of the absorption coefficient as a function of wavenumber, as well as generation of data files containing the coefficient and the transmittance functions.

For the foreign gas broadening study done in this research, the proper broadening function is a Lorentz function. Therefore, the Voigt function-fitting routine developed by Majorana and Copeland (ref. 5) cannot be used efficiently. A new program, BROAD (listed in the Appendix) was developed to fit in a nonlinear least squares sense a Lorentzian to the absorption coefficient: that is, a fit of the data is made to the function

$$y = A4 + \frac{A1}{(\omega - A2)^2 + \left(\frac{A3}{2}\right)^2} \qquad (1)$$

where A1 is the numerator of the Lorentzian, A2 is the center frequency (in cm^{-1}), A3 is the half-width at half maximum (HWHM) of the profile, and A4 is the background.

The program BROAD makes extensive use of the data-fitting routines developed by Bevington (ref. 8) and provides a file for plotting its fitted function together with the data for the user. The program begins by asking the user the name of the input data file. The program reports the number of

data points, the date the data was taken, the total (O_3 + N_2) pressure in torr, and the minimum and maximum values of the absorption coefficient. The subroutine CHOP is called, and the user may reduce the size on high and low wavenumber ends of the spectrum to analyze. The total wavenumber interval across the data is reported, and the user may normalize the data if needed. The function AREA is called, and the integral of the absorption coefficient over wavenumber is calculated, i.e., the strength in units of $cm^{-2}torr^{-1}$. The user may select any of three different procedures in which to weight the data during the fitting procedure (MODE = +1,0,-1) which correspond to the Bevington weight convention (ref. 8).

The program BROAD was designed to fit Lorentzians to either convex or concave data sets, i.e., A4 near zero or A4 maximum. The program automatically detects each case and, assuming only one spectral line, then makes initial guesses at the parameters A1, A2, A3, A4 and at their initial movements DELTAA(1-4). These are reported to the user. The program uses the grid-search method, subroutine GRIDLS, and the DO loop 100 is entered. After each exit from GRIDLS, the reduced chi square statistic is compared with the previous value. If it has not changed by more than two percent, iteration is stopped and the program reports the final chi square, the number of iterations, the final values of the parameters A1 to A4, and estimates of their errors. Finally, the total pressure in torr and the half-width at half maximum in both cm^{-1} and MHz are reported. The user may then select to see a recap of the data and the best fit and plot such as a graphics terminal. An example output of program BROAD is shown in the appendix.

RESULTS

These results are the first report to date of ozone line width broadening in the $\nu 1$ band using N_2 as the foreign gas. Table 1 lists the N_2 pressure, the fitted half-widths, and the line strengths for the case where the initial ozone pressure was 3.16 torr. Figures 2 through 10 show the Lorentz fit to the absorption coefficient from the program BROAD.

The half-widths as a function of pressure are shown in figure 11. We find they can be represented by

$$\delta(\text{HWHM in MHz}) = A + B\,p_{N_2} \tag{2}$$

with

$$A = 47.4 \pm 6.3 \text{ MHz}$$

and

$$B = 1.730 \pm 0.01 \text{ MHz/torr}$$

with a linear correlation coefficient of 0.9897. The intercept value 47.4 ± 5.3 MHz corresponds to the $O_3 - O_3$ broadened width at 3.16 torr O_3. This self-broadening half-width compares well with the results of Majorana et al. (ref. 1), who found a width of 44.52 MHz. The two values agree well within error bounds. Any significant difference could be traced to frequency instability in the diode laser.

The strength of the absorption line is defined as the integral over wavenumber of the absorption coefficient; that is, strength S is given by

$$S(\text{cm}^{-2}\,\text{torr}^{-1}) = \quad k(\nu)d\nu \tag{3}$$

Generally, S is a constant for self-broadened data; however, we find S to be N_2 pressure dependent. Figure 12 shows the strength for this transition as a function of N_2 pressure. We find that the strength can be represented as a power function of the N_2 pressure, i.e., $S = Ap_{N_2}^{B}$, where A = 1.334 × 10^{-4} and B = 1.314 ± 0.049 with a correlation coefficient of -0.9957. Since -1.34 is essentially -4/3, then we find the strength varies as pressure of nitrogen raised to the -4/3 power. This curious result may be due to several effects: chemical decomposition of O_3 due to collisions with N_2 or formation of weak Van de Waals molecules with N_2, i.e., $O_3 + N_2 \rightarrow O_3N_2$ and the resulting modification of residual ozone concentration.

APPENDIX

PROGRAM BROAD

This program is designed to perform the main data processing tasks as described in detail in the section "The Data and Its Analysis." This program is written in Fortran-10 and runs on a Dec System-10 time shared computer under the Tops10 operating system. Extensive use is made of the following data handling routines selected from those of Bevington (ref. 8) and are not listed here:

```
          GRIDLS(X,Y,SIGMAY,NPTS,NTERMS,MODE,A,DELTAA,SIGMAA,YFIT,
     CHISQR)

          INTEG(X,Y,NPTS,1,X1,X2,SUM)

          MATINV(ARRAY ,NTERMS,DET)

          FUNCTION FCHISQ(Y,SIGMAY,NPTS,NFREE,MODE,YFIT)

          FUNCTION AREA(X,Y,NPTS,NTERMS)
```

LISTING

```
      PROGRAM BROAD
C
C     WRITTEN BY
C     DR. G. E. COPELAND
C     DEPARTMENT OF PHYSICS AND GEOPHYSICAL SCIENCES
C     OLD DOMINION UNIVERSITY
C     NASA HETERODYNE GRANT
C
      DIMENSION YLABEL(16),XLABEL(10),TITLE(35),SIGMAX(400),
     1SIGMAY(400)
      DIMENSION X(400),Y(400),YFIT(400),A(4),SIGMAA(4)
      DIMENSION DELTAA(4)
      DOUBLE PRECISION FILE
C
C     SPEED OF LIGHT IN CM PER SECOND
C
      C=2.9979250E10
C
C     DATA FOR THE LABELS ON THE GRAPH
C
      DATA XLABEL/'W','A','V','E','N','U','M','B','E','R'/
```

```
      DATA YLABEL/'A','B','S','.',
     1'C','O','E','F','F','.','B','A','S','E',' ','E'/
      DATA TITLE/'O','3',' ','L','I','N','E',' ',' ','A','T','1','1',
     1'2','9','.','4','4','3','C','M','-','1',' ','L','O','R','E','N'
     2,'T','Z',' ','F','I','T'/
C
      DATA YLAB3/'R','E','S','I','D','U','A','L','S'/
      TYPE 92
92    FORMAT(' L O R E N T Z I A N FITTING FUNCTION')
      WRITE(5,10010)
      ACCEPT 10020 ,FILE
      OPEN(UNIT =21,DEVICE='DSK',ACCESS='SEQIN',FILE=FILE)
      READ(21,*)NPTS,K2,K3,K4,P3
      IF(NPTS.GT.400) TYPE 41
41    FORMAT('  TOO MANY DATA POINTS ENLARGE THE DIMENSIONS')
      IF(NPTS.GT. 400) STOP
      TYPE 222,NPTS
222   FORMAT('  NUMBER OF DATA PAIRS  =',I4)
      TYPE 451,K2,K3,K4
451   FORMAT(1X,' MONTH =',I2,' DAY =',I3,' YEAR =',I4)
C
      TYPE 4519,P3
4519  FORMAT(' PRESSURE IS ',F7.2,' TORR')
C
C     READ THE DATA IN THE FILE INTO X AND Y ARRAYS
C
      CALL READDT(X,Y,NPTS)
C
C
      DO 31 I=1,NPTS
C     TYPE 32 ,I,X(I),Y(I)
32    FORMAT( 1X,I3,1X,F8.3,1X,F8.3)
31    CONTINUE
C
C
      CLOSE(UNIT=21,DEVICE='DSK',ACCESS='SEQIN',FILE=FILE)
C
C
CALL ROUTINE TO CHOP OUT 1ST AND LAST OF DATA TO GET RID OF OUTER LINES
C
C
      CALL CHOP(NPTS,X,Y)
C
C
C
C     ASK IF DATA IS TO NORMALIZED
C
      TYPE 77
77    FORMAT('  DO YOU WANT THE DATA NORMALIZED?<Y=1,N=0>'$)
      ACCEPT *,ANNOR
      IF ( ANNOR .EQ. 0) GOTO 79
```

```
C
C       YES NORMALIZE IT
C
        ANSW=AREA(X,Y,NPTS,3)
C
C

C       SCALE THE Y ARRAY NOW
C
        DO 732 I=1,NPTS
732     Y(I)=Y(I)/ANSW
C
C
        TYPE 765,ANSW
765     FORMAT('  INTEGRAL OVER THE DATA IS =',1PE)
79      OPEN(UNIT=22,DEVICE='DSK',ACCESS='SEQOUT',FILE='PLTTEK.DAT')
        NSHET=1
        NGRP=2
        WRITE(22,10190) NSHET
C       INPUT MODE +1,0,-1.
C
C       MODE=+1 IS THE INSTRUMENTAL
C       MODE = -1 IS STATISTICAL
C       MODE =-1
C       MODE =0 NO WEIGHTING
C
40      WRITE(5,10100)
        MODE=-1
        ACCEPT *,MODE
C       CALCULATE MEAN IN XAND Y-
        YMEAN=0.0
        XMEAN=0.0
        DO 50 I=1,NPTS
        SIGMAX(I)=0.0
        XMEAN=X(I)+XMEAN
        SIGMAY(I)=0.0
        YMEAN=YMEAN+Y(I)
50      CONTINUE
        XMEAN=XMEAN/FLOAT(NPTS)
        YMEAN=YMEAN/FLOAT(NPTS)
C       CALCULATE 'SD' OF 'Y' AND 'SD' OF 'X' (SDY _SDX)
        SDX=0.0
        SDY=0.0
        DO 70 I=1,NPTS
        SDX=(X(I)-XMEAN)**2+SDX
        SDY=(Y(I)-YMEAN)**2+SDY
        SIGMAX(I) = SQRT( (X(I)-XMEAN)**2 )
        SIGMAY(I)= SQRT((Y(I)-YMEAN)**2)
70      CONTINUE
        SDX=SQRT(SDX/FLOAT(NPTS-1))
        SDY=SQRT(SDY/FLOAT(NPTS-1))
```

```
C       WE HAVE SDY _SDX TO PROVIDE START UP VALUES FOR
C       THE GRID SEARCH
C
        YMAX=Y(1)
        DO 80 I=2,NPTS
        IF( YMAX .LT. Y(I) ) YMAX=Y(I)
80      CONTINUE
        NTERMS=4
        YMIN=Y(1)
        DO 81 I=2,NPTS
        IF( YMIN .GT. Y(I) ) YMIN=Y(I)
81      CONTINUE
C
C
C       G U E S S   R O U T I N E
C
        A(4)=( Y(1) +Y(NPTS) )*0.5
C       TYPE *,YMIN,YMEAN,YMAX,XMIN,XMEAN,XMAX
        A(2)=XMEAN
C
        IF(Y(1) .LT. YMEAN ) GOTO 811
C
C               CURVE IS CONCAVE
        ICON=1
        TYPE 877
877     FORMAT('                CURVE IS CONCAVE')
        YMID=Y(1)-( Y(1)-YMIN)*0.5
        DO 992 I=1,NPTS
        IF( Y(I) .LT. YMID) XL=X(I)
        IF( Y(I) .LT. YMID) ILEFT=I
        IF( Y(I) .LT. YMID) GOTO 993
992     CONTINUE
        STOP '992'
993     DO 994 I=ILEFT,NPTS
        IF( Y(I).GT. YMID) XR=X(I)
        IF( Y(I) .GT. YMID) GOTO 995
994     CONTINUE
        STOP '994'
811     CONTINUE
C
CURVE IS CONVEX
        TYPE 878
878     FORMAT(' CURVE IS CONVEX')
C
        YMID=Y(1)+(YMAX-Y(1))*0.5
        DO 8121 I=1,NPTS
        IF( Y(I) .GT. YMID) XL=X(I)
        IF( Y(I) .GT. YMID) ILEFT=I
        IF( Y(I) .GT. YMID) GOTO 8131
8121    CONTINUE
        STOP '8121'
```

```
8131    DO 814 I=ILEFT,NPTS
        IF( Y(I) .LT. YMID) XR=X(I)
        IF( Y(I) .LT. YMID) GOTO 995
814     CONTINUE
        STOP '814'
995     A(3)=XR-XL
C
C       A3 IS FWHM
C
        A(1)=(0.25* A(3)**2+(XMEAN-A(2))**2)*( YMAX-A(4) +0.5)
        IF( Y(1).GT. YMIN) A(1)=-A(1)
C
C       GOT A1,A2,A3,A4
C

C       TYPE *,A
C
C       NOW HAVE FINISHED THE
C       GENERATION OF  GUESSES ON A1,A2,A3,A4 FOR A LORENTZIAN FUNCTION
C       Y=A4 + A1/( ( X-A2)**2+(  A3/2)**2)
C

        WRITE(5,10120)
        WRITE(5,10110)(I,A(I),I=1,NTERMS)
C       FINISHED STARTING VALUES
C       NOW FIND THE INCREMENTS ON A(1),A(2),A(3)
C       SET STEP SIZE IN MEAN = 6SDX/20
        DELTAA(3)=A(3)/10.
C       SET STEP SIZE ON COEFFICIENT A1
        DELTAA(1)=A(1)/10.
C       SET STEP SIZE ON COEFFICIENT A2
        DELTAA(2)=(XMEAN+SDX)/10.0
C       GIVE GUESS ON DELTAA(4)----BACKGOUND
        DELTAA(4)=A(4)/10.0
C
C       ENTER LOOP
C       ITERATE 20 TIMES AT MOST
        KNT=0
        DO 100 K=1,15
        CALL GRIDLS(X,Y,SIGMAY,NPTS,NTERMS,MODE,A,DELTAA,
     1      SIGMAA,YFIT,CHISQR)
        TYPE 887,K,CHISQR
        IF(K .GT. 1)  GOTO 90
        SAVE=CHISQR
        SAVIT=SAVE
        KNT=1
        GOTO 100
90      XCHI=100.0*(CHISQR-SAVE)/CHISQR
        IF( XCHI .GT. 0.0 )  GOTO 110
C
CRITERION OF CONVERGENCE IS CHISQR DOES NOT CHANGE BY 1 PER CENT
```

```
C
C       OR IF CHISQR IS LESS THAN 0.02 OF THE 1ST CHISQR FOUND
C
C       BEVINGTON PAGE 212
C
        IF(  ABS(XCHI)   .LT.  0.5 )  GOTO 110
        IF( CHISQR .LT. 0.020*SAVIT) GOTO 110
        SAVE = CHISQR
        KNT=KNT+1
100     CONTINUE
110     KNT=KNT+1
        WRITE(5,10130) KNT
C       RETURNED VALUES ARE A,SIGMAA,YFIT,CHISQR
          WRITE(5,10140)
        DO 120 I=1,NTERMS
        WRITE(5,10150),I,A(I),SIGMAA(I)
120     CONTINUE
        WRITE(5,10160),CHISQR
        WRITE(5,10161),P3
10161   FORMAT('    TOTAL PRESSURE IS =',F6.2,' TORR')
        A3K=A(3)*.5
        A3MHZ=A3K*C/1.E+6
        TYPE 345  ,A3K,A3MHZ
345     FORMAT(1X,'HWHM =',F9.6,' CM-1 OR ',F12.4' MHZ')
130     WRITE(5,10170)
C       ANS1=0
        ACCEPT *,ANS1
        IF(ANS1.EQ.1)GO TO 150
140     WRITE(5,10180)
        ACCEPT *,ANS2
        IF(ANS2.EQ.0)  STOP
        WRITE(22,10190) NGRP
        WRITE(22,10190),NPTS
        WRITE(22,10080)(YLABEL(I),I=1,16)
        WRITE(22,10080)(XLABEL(I),I=1,10)
        WRITE(22,10200)(TITLE(I),I=1,35)
        WRITE(22,3451),A3K,A3MHZ,P3
3451    FORMAT(1X,'HWHM ',F9.6,' CM-1 ',F7.2' MHZ P= 'F6.2' TORR')
C       OUTPUT TO TEKTRONIX PLOTTING FILE
C
        DO 812 I=1,NPTS
        WRITE(22,10220) X(I),Y(I)
812     CONTINUE
C
C       WRITE FITTED DATA AND GENERATE NEW X VALUES
C
C
C       WRITE OUT THESE X AND YFIT
        DO 813 I=1,NPTS
813     WRITE(22,10220) X(I),YFIT(I)
99      CONTINUE
```

```
        CLOSE(UNIT=22,DEVICE='DSK',ACCESS='SEQOUT',FILE='PLTTEK.DAT')
        STOP
C       OUTPUT A DATA MATRIX IN TERMINAL
150     CONTINUE
        Q=0.0
C
C       FIND AVG OF ABS(% ERROR)
C
        WRITE(5,10240)
        DO 88 I=1,NPTS,10
        Z=( (Y(I)-YFIT(I))/YFIT(I) )*100.0
        Q=Q+ABS(Z)
88      WRITE(5,10250)  X(I),Y(I),YFIT(I),Z
        Q=10.*Q/FLOAT(NPTS)
        WRITE(5,10230)Q
        WRITE(5,10240)
        GO TO 140
887     FORMAT(' FINISHED ITERATION  ',I2,' CHI SQ =',1PE)
10010   FORMAT(1X,'WHAT IS INPUT FILE NAME<CONTAINS OUTPUT FROM
QUICK>?')
10020   FORMAT(A10)
10060     FORMAT(I)
10080   FORMAT(40A1)
10090   FORMAT(1X,40A1)
10100   FORMAT(1X,'WHICH MODE DO YOU WISH TO FIT DATA',/,
     1      1X,'+1=INSTRUMENTAL FITS= 1/VARIANCE',/,
     2      1X,'0= NO WGHT',/,
     3      1X,' -1= STATISTICAL=1/Y = ',/,1X,'?'$)
10110   FORMAT(5X,' A(',I1,' ) =',1PE)
10120   FORMAT(10X,' S T A R T  U P  V A L U E S')
10130   FORMAT(1X,'THERE WERE ',I3,' ITERATIONS')
10140   FORMAT(1X,'USING Y=A4+A1/( (X-A2)**2 + 0.25*A3 **2)
     1',/,1X,  'YOU OBTAIN:')
10150      FORMAT(5X,'A(',I1,') =',1PE,'+/- ',1PE)
10160   FORMAT(5X,'CHI SQUARED = ',1PE)
10170   FORMAT(1X,/,1X,'DO YOU WANT A DATA RECAP? YES=1,NO=0?'$)
10180   FORMAT(2X,'DO YOU WANT TO PLOT DATA ON GRAPHICS ?(YES=1,NO=0)'$)
10190   FORMAT(2X,I)
10200   FORMAT(40A1)
10210   FORMAT(5X,'A1-4=',4(1X,1PE9.2) )
10220   FORMAT(2X,1PE,2X,1PE)
10230   FORMAT(1X,'MEAN OF THE ABSOLUTE VALUE OF THE % ERROR =',F)
10240   FORMAT(2X,/,/,8X,'X-DATA',8X,'Y-DATA',8X,
     1'YFIT',8X,'PER CENT DIFF')
10250   FORMAT(1X,3(1PE,3X),0PF10.2)
        END
C
C-----------------------------------------------------------------
        FUNCTION FUNCTN(X,I,A)
C
C
```

```
C               TAKEN FROM
C         DATA REDUCTION AND ERROR ANALYSIS
C               FOR THE
C         PHYSICAL SCIENCES
C               BY
C         PHILIP R. BEVINGTON
C         MCGRAW-HILL BOOK CO 1969
C         PAGE 214
C
C
C         G E COPELAND    JUNE  1980
C         DEPARTMENT OF PHYSICS AND GEOPHYSICAL SCIENCES
C               OLD DOMINION UNIVERSITY
C               NORFOLK, VA. 23508
C
C
C
C         PURE LORENTZIAN FUNCTION
C
C         Y=A4+(A1)/(  (X-A2)**2 +(A3/2)**2  )
C
C
C         PLUS A BACKGROUND
C
          DIMENSION X(1),A(1)
10        XI=X(I)
30        Z=XI-A(2)
          Z2=Z*Z
          FUNCTN=A(1)/(Z2+(A(3)*A(3)*0.25))
          FUNCTN=FUNCTN+A(4)
50        RETURN
          END
C
C
C-----------------------------------------------------------------
C
          SUBROUTINE READDT(X,Y,N)
          DIMENSION X(1),Y(1)
C10       READ(21,211)KK,N,K2,K3,K4,K10,TAPENO,P3
C211      FORMAT(1X,I2,1X,I4,1X,3(I2,1X),I1,1X,A5,1X,F)
          READ(21,END=22,*)( (X(I),Y(I),I=J,J+4),J=1,N,5)
334       FORMAT(10(1X,1PE8.2) )
C         WRITE(5,334)( (X(I),Y(I),I=J,J+4),J=1,N,5)
          RETURN
22        CONTINUE
          TYPE 33
33        FORMAT(' RAN OUT OF DATA IN READDT---RECAP FOLLOWS')
          TYPE 34 ,N
34        FORMAT('  NUMEER OF DATA POINTS =',I)
          WRITE(5,*)( (X(I),Y(I),I=J,J+4),J=1,N,5)
          RETURN
```

```
      END
C
C-----------------------------------------------------------------
C
      SUBROUTINE CHOP(N,X,Y)
      DIMENSION X(1),Y(1)
      DIMENSION XSAV(400),YSAV(400)
C
C     CHOP OUT PARTS OF THE ARRAY AND REPLACE IT IN THE ORGINAL ARRAYS
C
      NSAV=N
      DO 10 I=1,NSAV
      XSAV(I)=X(I)
10    YSAV(I)=Y(I)
      YMIN=Y(1)

      DO 20 I=2,NSAV
      IF(YMIN .GT.Y(I)) IMIN=I
      IF(YMIN .GT.Y(I)) YMIN=Y(I)
20    CONTINUE
      TYPE 100 ,YMIN,IMIN
100   FORMAT(' MINIMUM VALUE OF Y ='F,' AT POINT ',I3)
      YMAX=Y(1)
      DO 201 I=2,NSAV
      IF( Y(I) .GT. YMAX) IMAX=I
      IF( Y(I) .GT. YMAX) YMAX=Y(I)
201   CONTINUE
      TYPE 2011,YMAX,IMAX
2011  FORMAT(' MAXIMUM VALUE OF Y ='F,' AT POINT ',I3)
109   TYPE 110
110   FORMAT(' DO YOU WANT TO CHOP PARTS OF THE ARRAY OFF?<Y=1,NO=0>')
      ACCEPT *,ANS
      IF(ANS.EQ.0) RETURN
      IF(ANS.EQ.1) GOTO 150
      GOTO 109
150   CONTINUE
      TYPE 160
160   FORMAT(' INPUT   OF LEFT DATA POINT TO START NEW ARRAY?'$)
      ACCEPT *,IST
      TYPE 161
161   FORMAT(' INPUT   OF DATA POINT ON RIGHT TO STOP THE ARRAY?'$)
      ACCEPT *,ISP
      IF( ISP.LT.IST) GOTO 109
C
C     REPORT THE DIFFERENCE IN FREQUENCY BETWEEN THE 2 LIMITS
C
      DIFF=X(ISP)-X(IST)
      TYPE 1601,DIFF
1601  FORMAT(' WAVENUMBER CHANGE ACROSS THIS SAMPLE =',F8.7,' CM-1')
      DO 30 I=IST,ISP
      X(I-IST+1)=XSAV(I)
```

```
30        Y(I-IST+1)=YSAV(I)
          N=ISP-IST
          RETURN
          END
```

```
   RUN BROAD

L O R E N T Z I A N FITTING FUNCTION
WHAT IS INPUT FILE NAME<CONTAINS OUTPUT FROM EARL>?
FIL5
 NUMBER OF DATA PAIRS   = 200
 MONTH =12 DAY = 19 YEAR =  79
PRESSURE IS   53.59 TORR
MINIMUM VALUE OF Y =      -0.0000024 AT POINT 180
MAXIMUM VALUE OF Y =       0.0000723 AT POINT  93
DO YOU WANT TO CHOP PARTS OF THE ARRAY OFF?<Y=1,NO=0>
1
INPUT # OF LEFT DATA POINT TO START NEW ARRAY?
20
INPUT # OF DATA POINT ON RIGHT TO STOP THE ARRAY?
180
WAVENUMBER CHANGE ACROSS THIS SAMPLE =.0484009 CM-1
 DO YOU WANT THE DATA NORMALIZED?<Y=1,N=0>
1
 INTEGRAL OVER THE DATA IS =  8.1862793E-07
WHICH MODE DO YOU WISH TO FIT DATA
+1=INSTRUMENTAL FITS= 1/VARIANCE
0= NO WGHT
 -1= STATISTICAL=1/Y =
?
0
CURVE IS CONVEX
          S T A R T  U P  V A L U E S
     A(1 ) = -1.5973438E-03
     A(2 ) =  1.1294275E+03
     A(3 ) =  8.4991455E-03
     A(4 ) =  3.6646686E-01
FINISHED ITERATION # 1 CHI SQ =   1.2879837E+02
FINISHED ITERATION # 2 CHI SQ =   1.2755936E+02
FINISHED ITERATION # 3 CHI SQ =   1.2667750E+02
FINISHED ITERATION # 4 CHI SQ =   1.2597696E+02
FINISHED ITERATION # 5 CHI SQ =   1.2537410E+02
THERE WERE    5 ITERATIONS
USING Y=A4+A1/( (X-A2)**2 + 0.25*A3 **2)
YOU OBTAIN:
    A(1) =  1.6568207E-03+/-  -4.1651741E-06
    A(2) =  1.1294275E+03+/-   3.5054553E-03
    A(3) =  9.0509854E-03+/-   1.4426374E-05
    A(4) = -3.5671993E-01+/-   7.9056752E-02
    CHI SQUARED =    1.2537410E+02
  TOTAL PRESSURE IS = 53.59 TORR
HWHM = 0.004525 CM-1 OR     135.6709 MHZ
```

```
DO YOU WANT A DATA RECAP? YES=1,NO=0?
0
 DO YOU WANT TO PLOT DATA ON GRAPHICS ?(YES=1,NO=0)
0
STOP

END OF EXECUTION
CPU TIME: 1.46  ELAPSED TIME: 1:3.32
EXIT
```

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Table 1. Half-widths (HWHM) and strengths vs. N_2 pressure for O_3 broadened with O_3 pressure = 3.16 torr at 285 K.

SN_2 Pressure (torr)	Half-widths (mKaysers)	(MHz)	Strengths[a,b] $cm^{-2}\,torr^{-1}$
0.0	1.615	48.43	4.602(-5)
10.15	1.929	57.83	6.738(-5)
15.10	2.290	68.66	4.043(-6)
19.95	2.784	83.47	2.385(-6)
30.30	3.819	114.5	1.435(-6)
50.43	4.491	134.6	7.892(-7)
60.48	4.945	148.3	5.945(-7)
90.80	7.600	227.8	3.853(-7)
100.6	6.834	205.0	3.438(-7)

[a]integration over 55 mKaysers
[b]Numbers in ( ) are powers of 10

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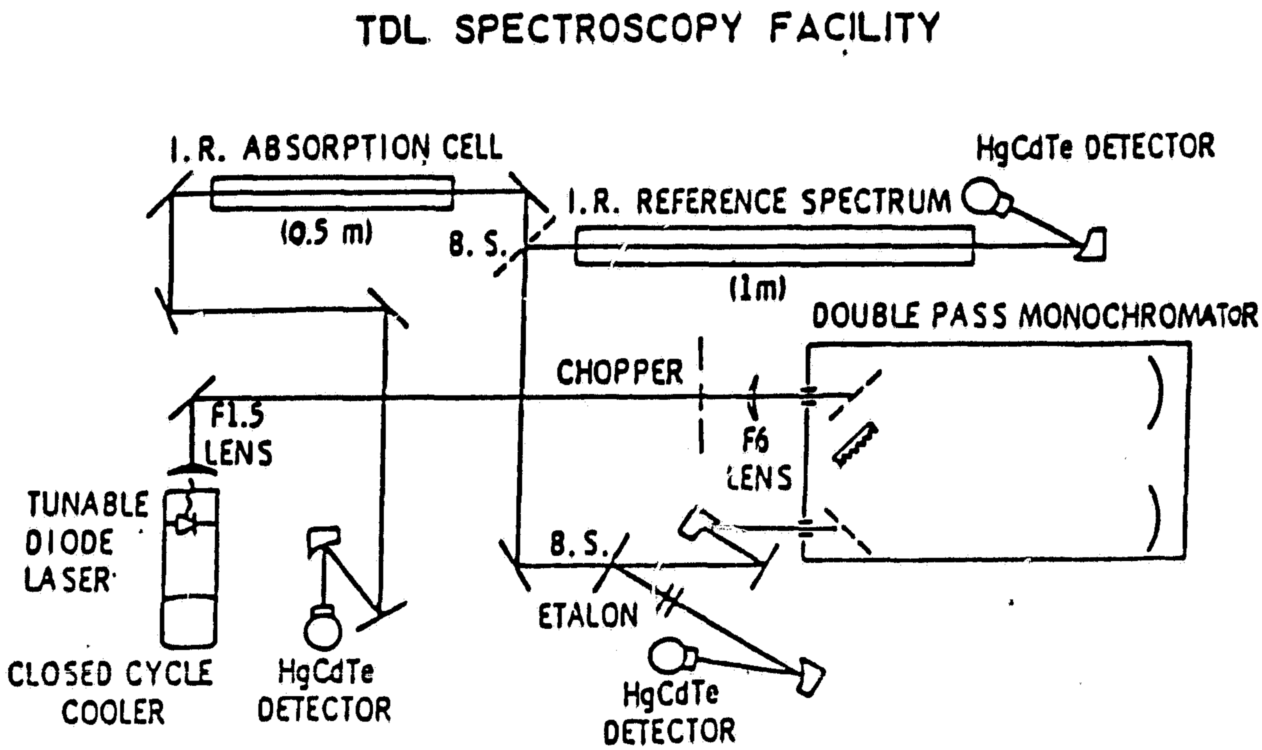

Figure 1. Optical setup for simultaneous measurement of reference gas spectrum, test gas spectrum and etalon tuning curve.

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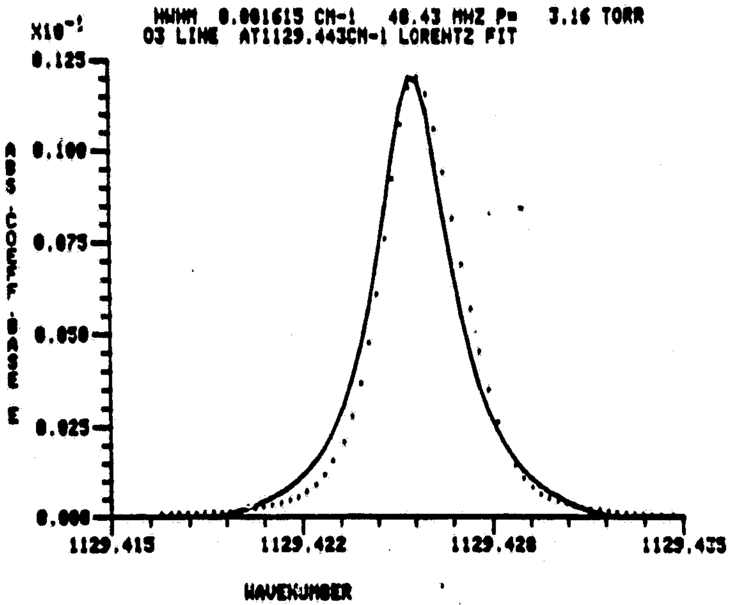

Figure 2. Absorption coefficient vs. wavenumber at pressure = 3.16 torr.

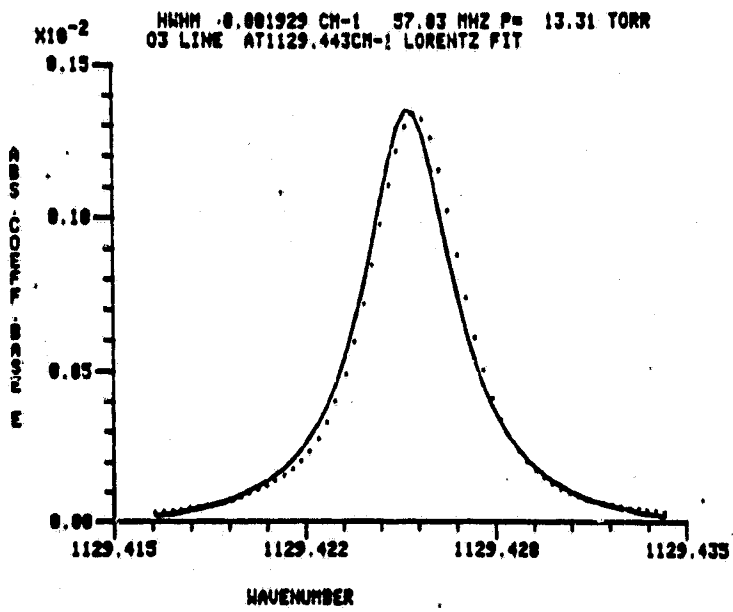

Figure. 3. Absorption coefficient vs. wavenumber at pressure = 13.31 torr.

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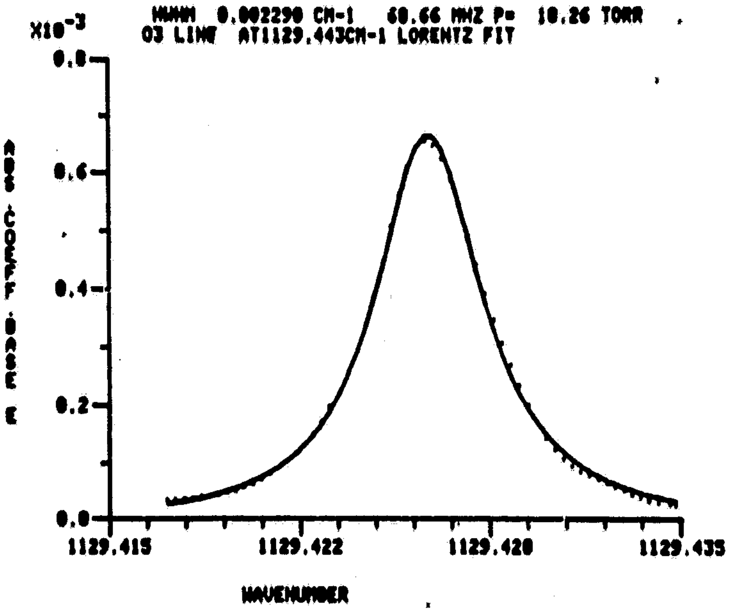

Figure 4. Absorption coefficient vs. wavenumber at pressure = 18.26 torr.

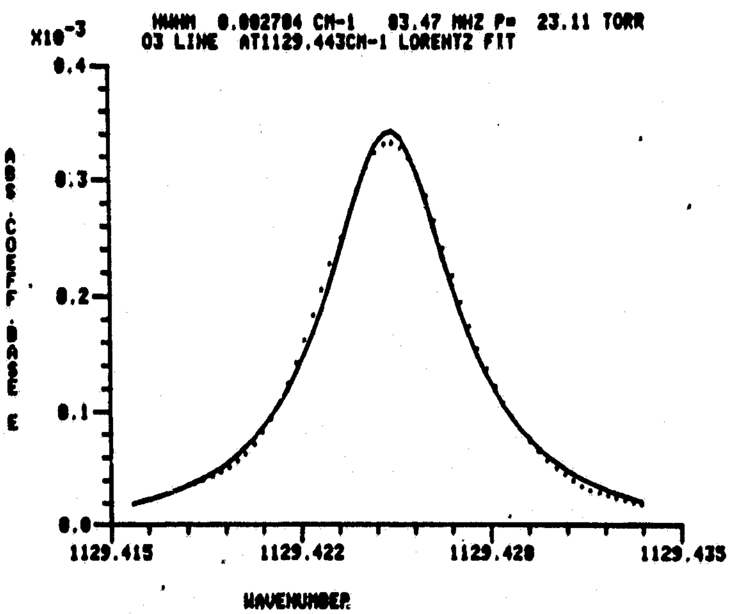

Figure 5. Absorption coefficient vs. wavenumber at pressure = 23.11 torr.

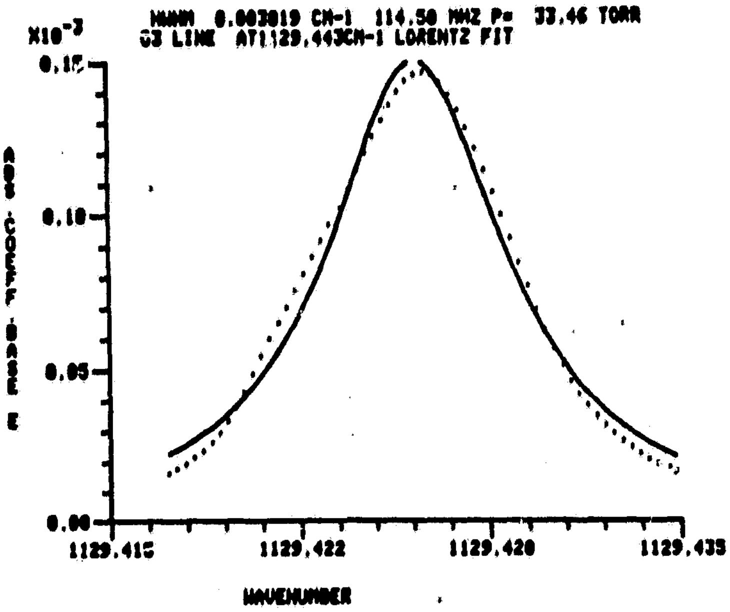

Figure 6. Absorption coefficient vs. wavenumber at pressure = 33.46 torr.

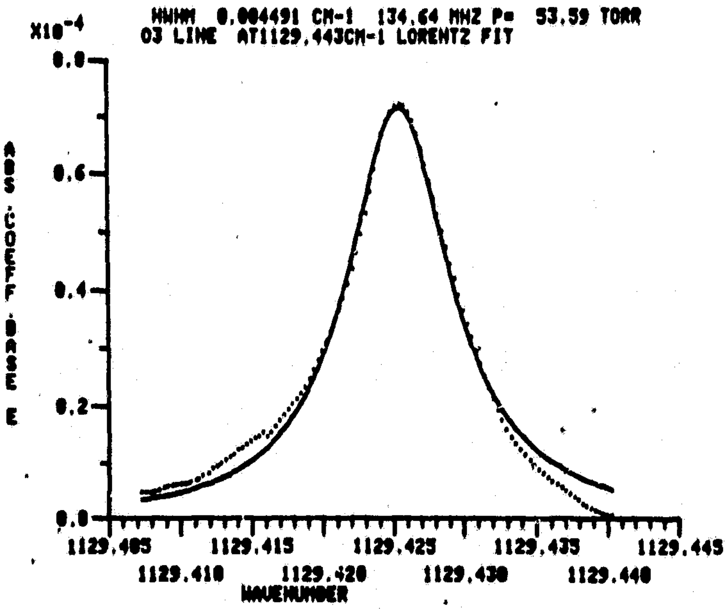

Figure 7. Absorption coefficient vs. wavenumber at pressure = 53.59 torr.

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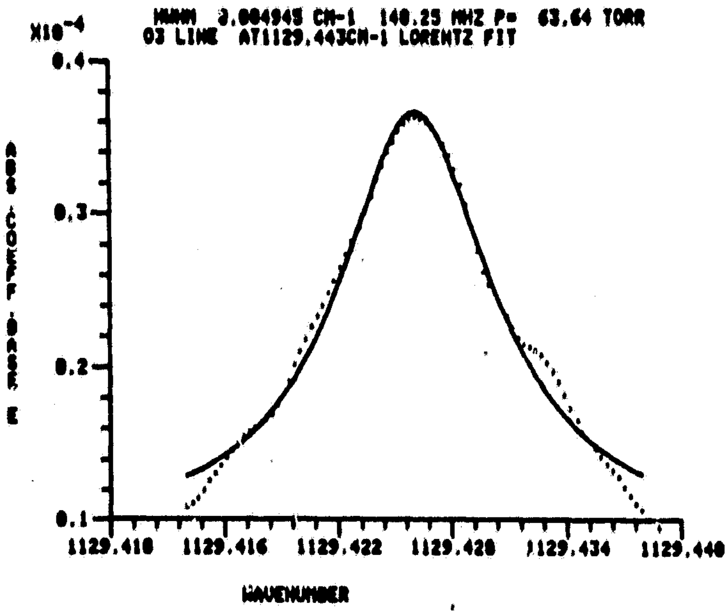

Figure 8. Absorption coefficient vs. wavenumber at pressure = 63.64 torr.

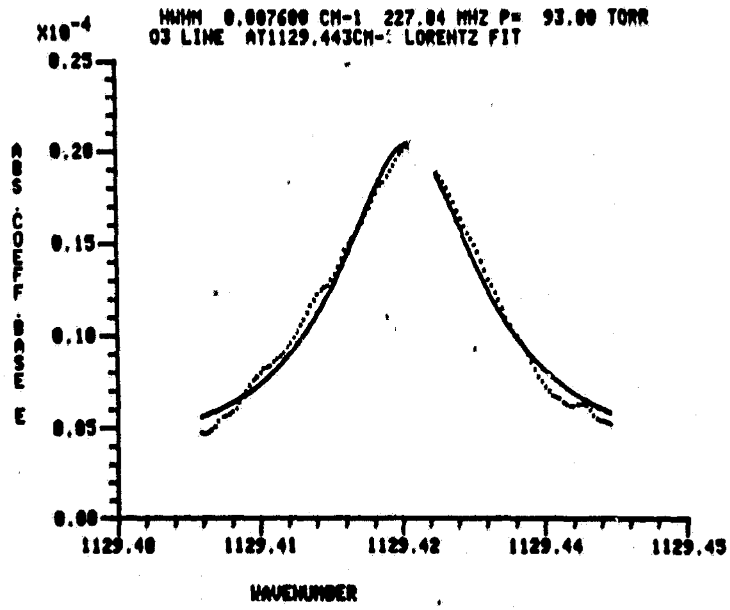

Figure 9. Absorption coefficient vs. wavenumber at pressure = 93.80 torr.

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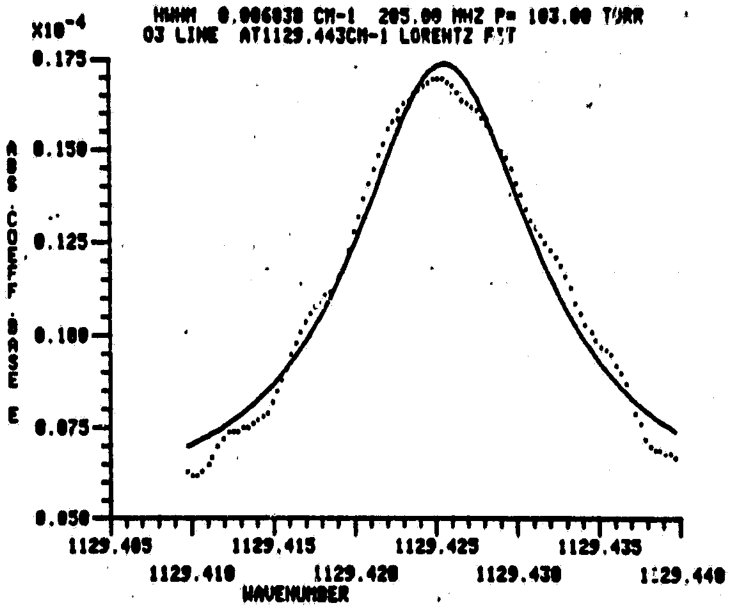

Figure 10. Absorption coefficient vs. wavenumber at pressure = 103.80 torr.

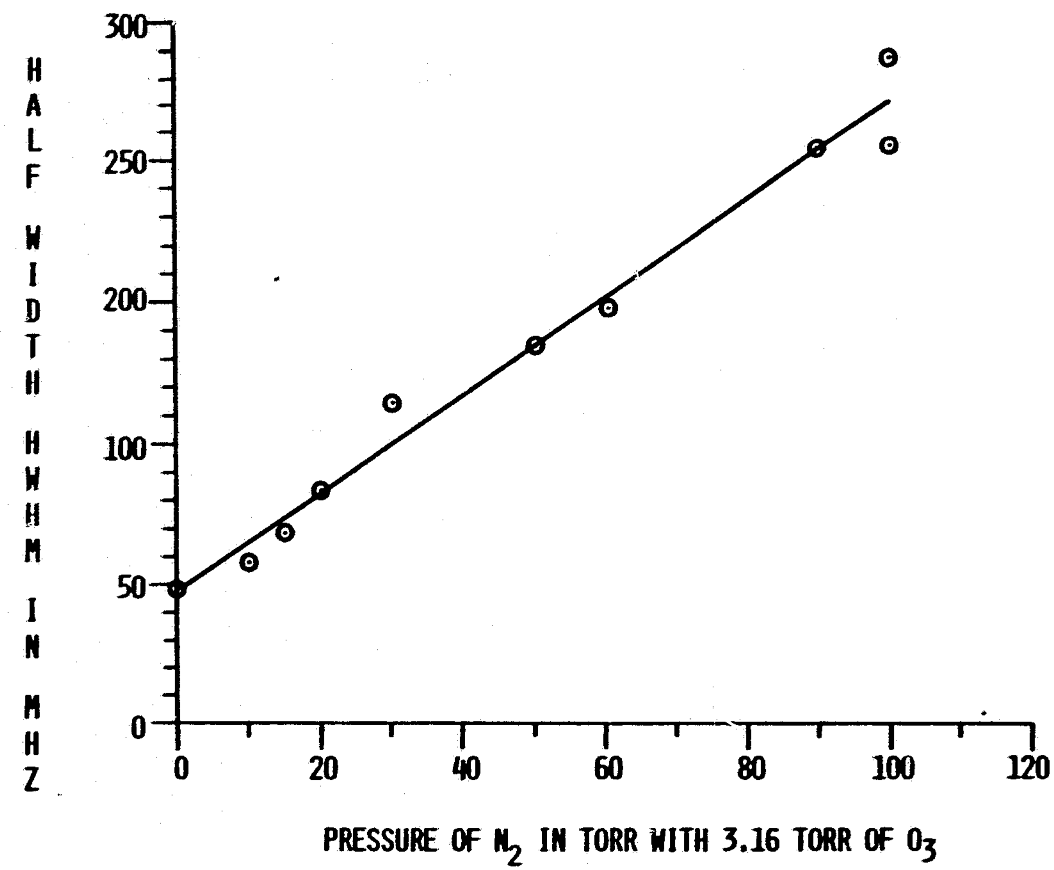

Figure 11. Half-width vs. pressure of N_2 with 3.16 torr of O_3.

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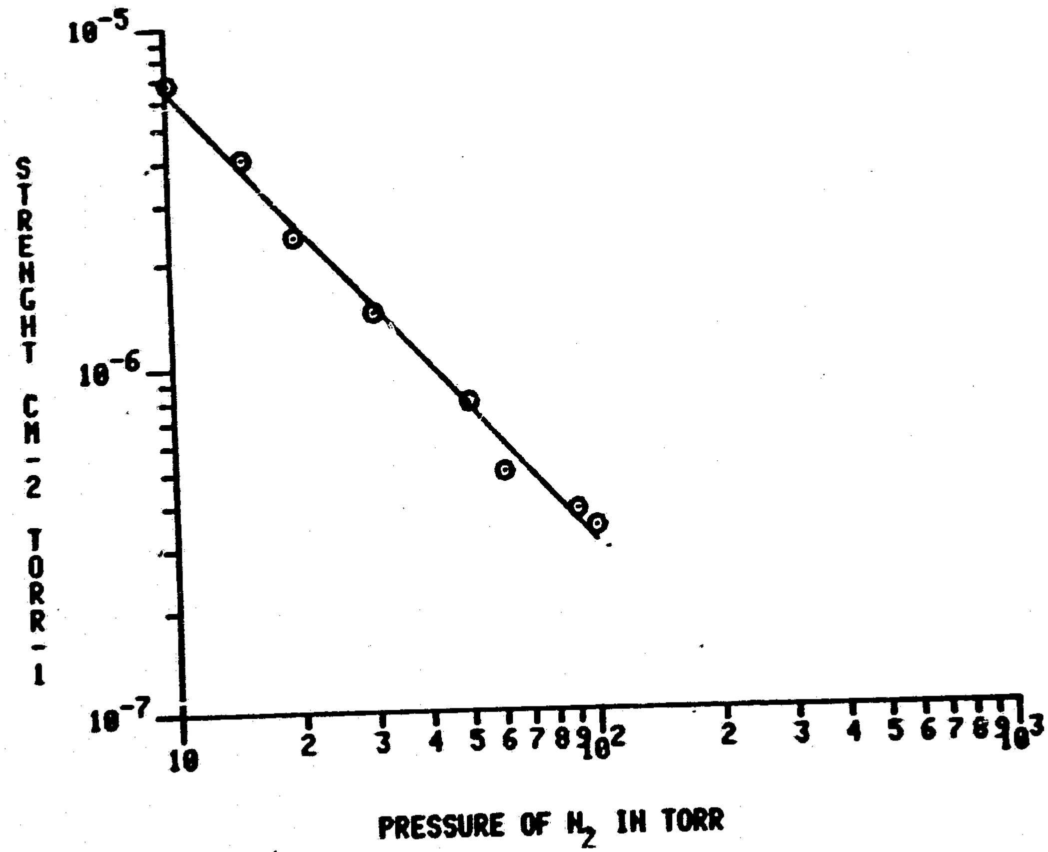

Figure 12. Strength vs. pressure of N_2 for O_3 = 3.16 torr.